Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Matzat, E. (1972). *Acta Cryst.* B**28**, 415–418.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.
Ribar, B., Stankovic, S. & Halasi, R. (1976). *Cryst. Struct. Commun.* **5**, 919–922.
Ribar, B., Stankovic, S., Herak, R., Halasi, R. & Djuric, S. (1974). *Cryst. Struct. Commun.* **3**, 669–672.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Acta Cryst. (1994). C**50**, 827–829

t-3-Isopropyl-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one, $C_{20}H_{24}N_2O$

K. Ravikumar

Indian Institute of Chemical Technology,
Hyderabad 500 007, India

S. S. Rajan

Department of Crystallography and Biophysics,
University of Madras, Madras 600 025, India

V. Parthasarathi* and A. Thiruvalluvar

Department of Physics, Bharathidasan University,
Tiruchirapalli 620 024, India

R. Jeyaraman and U. P. Senthilkumar

Department of Chemistry, Bharathidasan University,
Tiruchirapalli 620 024, India

(*Received* 20 *May* 1993; *accepted* 7 *October* 1993)

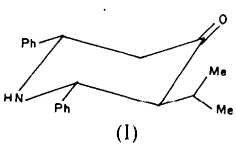
Abstract

The diazepine ring adopts a slightly distorted chair conformation. The phenyl substituents adopt equatorial orientations. The unsymmetrical distortion arises from the torsional strains between the phenyl and isopropyl groups. The compound exists as a dimer exhibiting intermolecular N—H···O hydrogen bonding.

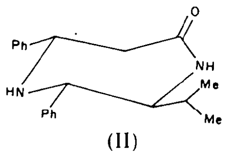
Comment

A wide range of diazepines have been identified as potential drugs for various diseases (Hamor & Martin, 1984). Most of them contain benzene rings fused to the diazepine ring at the 2,3 and/or 6,7 position. The fusion of the aromatic hydrocarbons makes the boat form of the diazepines more stable. We have been interested in the conformational effect of substituting (rather than fusing) the phenyl rings to the 2 and 7 positions of the diazepine ring.

The Beckmann rearrangement of the oxime derivative of the 3-isopropylpiperidone (I) has been reported to afford the diazepine (II) exclusively, though there are two possibilities for the ring opening to afford two isomers, *viz.* the 3-isopropyldiazepinone (II) and a 6-isopropyldiazepinone (Baliah, Lakshmanan & Pandiarajan, 1978). Schmidt reaction of the piperidone (I) has also been reported (Mohan, 1985) to yield the diazepine (II). Though the determination of the regiochemistry of migration may appear to be trivial, the formation of an abnormal product in the Schmidt rearrangement of the related ketone, namely 2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one, justifies the need for the confirmation of the regiochemistry. Instead of migration of the α bond alone, both α and β bonds were found to migrate (Senthilkumar & Jeyaraman, 1993). We were interested in determining whether there has been any configurational change during the Schmidt rearrangement. For this purpose, *t*-3-isopropyl-*r*-2,-*c*-6-diphenylpiperidone (I) was prepared and converted to its hydrochloride. The hydrochloride (5.11 g, 15.53 mmol) was dissolved in concentrated H_2SO_4 (25 ml) and one equivalent of sodium azide (1.24 g, 19.07 mmol) was added in small portions for a period of 1 h. After the addition was over, the solution was stirred for another hour and poured slowly onto crushed ice and basified (pH 8) with cold concentrated NaOH solution. The precipitated solid was separated by filtration through a Buchner funnel, washed several times to remove excess sodium hydroxide and dried. Recrystallization from benzene followed by ethanol afforded colourless crystals of *t*-3-isopropyl-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one (II); m.p. 461–462 K [literature value 461 K (Baliah, Lakshmanan & Pandiarajan, 1978)].



(I)



(II)

Both the phenyl groups of the title compound are *trans* to the isopropyl group as in the parent piperidone (I). This observation indicates that the relative geometry of the substituents is preserved during the Schmidt reaction, thus confirming it to be an intramolecular rearrangement.

© 1994 International Union of Crystallography
Printed in Great Britain - all rights reserved

Acta Crystallographica Section C
ISSN 0108-2701 © 1994

Fig. 1 shows a perspective view of the molecule with atomic numbering. The phenyl ring at C2 is perpendicular [86.4 (1)°] to the dynamically averaged plane of the diazepine ring and the torsion angle N1—C2—C21—C22 is −63.6 (3)°. The phenyl ring at C7 is slightly tilted [57.6(1)°] and the torsion angle N1—C7—C71—C72 is −146.5 (2)°. The perpendicular orientation of the phenyl ring at C2 could arise from the repulsion between the phenyl ring and the isopropyl group at C3.

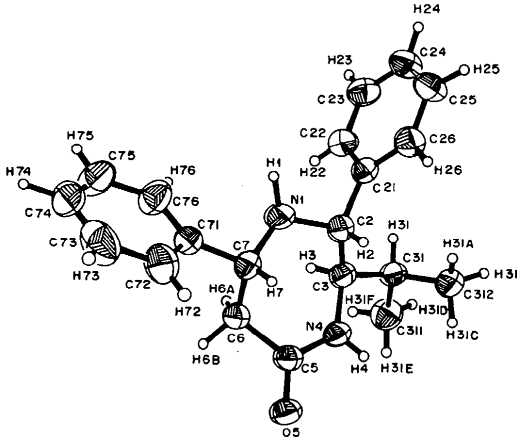
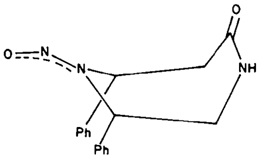


Fig. 1. Perspective view of the molecule with atomic numbering system.

The torsion angle C3—N4—C5—C6 is −7.1 (4)°. This indicates nearly planar geometry for C3, N4, C5 and C6, suggesting the delocalization of the N-atom lone pair over the carbonyl group. The atoms H4, N4, C5, C6 and H6*B* are in a plane as observed from the torsion angles of 178.8 (3) and 174.3 (2)° for H6*B*—C6—C5—N4 and C6—C5—N4—H4, respectively. The three angles C7—N1—C2, C7—N1—H1 and C2—N1—H1 add up to 337.0 (2)° and the displacement of N1 from the plane defined by the atoms N1, C7, C2 and H1 is −0.278 (2) Å, while the deviation of the other atoms is less than 0.1 Å, showing essentially pyramidal geometry at N1.

The nitroso derivative (III) of the analogous diazepinone (Priya, Shamala, Viswamitra, Senthilkumar & Jeyaraman, 1992) has been reported to adopt the boat conformation, while the title compound (II) adopts a distorted chair conformation. Such a change in the conformation of the ring from chair to boat arises as a result of the severe allylic strain exerted by the nitroso group on the phenyl groups. Consequently the phenyl groups adopt pseudo axial orientations in the boat form of the ring in (III). The crystal structure of the nitrosodiazepinone (III) has been found to be stabilized by *polymeric* association through hydrogen bonding between the carbonyl group and H4 (N—H···O) as well as H7 (C—H···O), while the crystal structure of the diazepinone (II) is stabilized by *dimeric* association through hydrogen bonding between C=O and N4—H4 as shown in Fig. 2. The NMR spectrum of the title compound shows a vicinal coupling constant of 2.2 Hz between NH and H3, indicative of an associated form in solution (Senthilkumar, Jeyaraman, Murray & Singh, 1992).



(III)

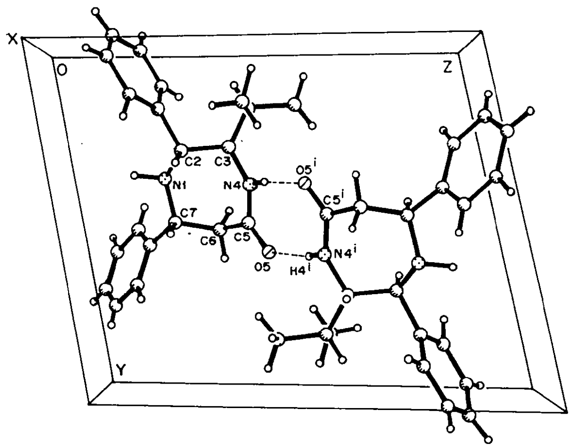


Fig. 2. Crystal packing showing the hydrogen bond in the dimer, N4—H4···O5ⁱ: N4···O5ⁱ = 2.983 (3) Å and N4—H4···O5ⁱ = 171.6 (2)° [symmetry code: (i) $-x+1$, $-y+1$, $-z+1$].

Experimental

Crystal data

$C_{20}H_{24}N_2O$
$M_r = 308.4$
Triclinic
$P\overline{1}$
$a = 5.903$ (2) Å
$b = 11.143$ (5) Å
$c = 13.912$ (4) Å
$\alpha = 77.72$ (3)°
$\beta = 82.83$ (2)°
$\gamma = 83.12$ (3)°
$V = 883.0$ (6) Å^3
$Z = 2$

$D_x = 1.16$ Mg m^{-3}
$D_m = 1.17$ Mg m^{-3}
D_m measured by flotation in CCl_4/petroleum ether
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 30$–55°
$\mu = 0.526$ mm^{-1}
$T = 299$ K
Prismatic
0.79 × 0.35 × 0.26 mm
Colourless

Data collection

Siemens *R*3*m*/*V* diffractometer
2θ-θ scans
Absorption correction: none
4441 measured reflections
2226 independent reflections
1941 observed reflections [$F > 6.0\sigma(F)$]
$R_{\text{int}} = 0.052$
$\theta_{\max} = 55°$
$h = -6 \rightarrow 6$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 100 reflections intensity variation: none

Refinement

Refinement on *F*
$R = 0.059$
$wR = 0.071$
$S = 1.55$
1941 reflections
209 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0010F^2]$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: $F^* = F[1 - (0.0001\chi \times F^2/\sin\theta)]$
Extinction coefficient: $\chi = 0.00637$
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	0.1940 (3)	0.3806 (2)	0.2297 (1)	0.048 (1)
C2	0.3721 (3)	0.3007 (2)	0.2870 (2)	0.043 (1)
C3	0.3005 (3)	0.2894 (2)	0.3988 (2)	0.039 (1)
N4	0.3464 (3)	0.4005 (1)	0.4316 (1)	0.045 (1)
C5	0.2344 (4)	0.5120 (2)	0.4096 (2)	0.050 (1)
C6	0.0615 (4)	0.5322 (2)	0.3358 (2)	0.050 (1)
C7	0.1701 (3)	0.5113 (3)	0.2335 (2)	0.045 (1)
C21	0.4045 (3)	0.1801 (2)	0.2513 (2)	0.041 (1)
C22	0.2264 (4)	0.1034 (2)	0.2646 (2)	0.054 (1)
C23	0.2558 (4)	−0.0046 (2)	0.2298 (2)	0.064 (1)
C24	0.4588 (5)	−0.0375 (2)	0.1790 (2)	0.066 (1)
C25	0.6336 (4)	0.0355 (2)	0.1645 (2)	0.063 (1)
C26	0.6076 (4)	0.1444 (2)	0.2004 (2)	0.051 (1)
C31	0.4133 (3)	0.1761 (2)	0.4645 (2)	0.044 (1)
C311	0.3142 (4)	0.1663 (2)	0.5719 (2)	0.059 (1)
C312	0.6741 (4)	0.1708 (2)	0.4539 (2)	0.053 (1)
O5	0.2770 (3)	0.5984 (1)	0.4443 (1)	0.073 (1)
C71	0.0266 (3)	0.5829 (2)	0.1540 (2)	0.046 (1)
C72	0.0719 (4)	0.7031 (2)	0.1076 (2)	0.064 (1)
C73	−0.0634 (6)	0.7717 (2)	0.0386 (2)	0.081 (1)
C74	−0.2428 (5)	0.7269 (3)	0.0120 (2)	0.075 (1)
C75	−0.2911 (5)	0.6095 (3)	0.0564 (2)	0.091 (1)
C76	−0.1572 (4)	0.5367 (2)	0.1258 (2)	0.060 (1)

Table 2. *Selected geometric parameters* (Å, °)

N1—C2	1.489 (3)	C22—C23	1.375 (4)
N1—C7	1.458 (3)	C23—C24	1.365 (4)
C2—C3	1.542 (4)	C24—C25	1.359 (4)
C2—C21	1.512 (4)	C25—C26	1.393 (4)
C3—N4	1.472 (3)	C31—C311	1.521 (4)
C3—C31	1.527 (3)	C31—C312	1.523 (3)
N4—C5	1.329 (3)	C71—C72	1.399 (3)
C5—C6	1.502 (4)	C71—C76	1.386 (4)
C5—O5	1.228 (3)	C72—C73	1.370 (4)
C6—C7	1.539 (4)	C73—C74	1.346 (5)
C7—C71	1.508 (3)	C74—C75	1.370 (5)
C21—C22	1.403 (3)	C75—C76	1.385 (4)
C21—C26	1.375 (3)		
C2—N1—C7	116.7 (2)	N4—C5—C6	118.0 (2)
N1—C2—C21	106.3 (2)	C6—C5—O5	120.2 (2)
N1—C2—C3	110.0 (2)	C5—C6—C7	112.4 (2)
C3—C2—C21	115.0 (2)	N1—C7—C6	111.0 (2)
C2—C3—C31	114.7 (2)	C6—C7—C71	110.3 (2)
C2—C3—N4	110.6 (2)	N1—C7—C71	109.7 (2)
N4—C3—C31	108.7 (2)	C3—C31—C312	113.4 (2)
C3—N4—C5	126.2 (2)	C3—C31—C311	110.9 (2)
N4—C5—O5	121.7 (2)	C311—C31—C312	111.6 (2)
C2—N1—C7—C71	166.5 (2)	C2—C3—N4—C5	70.2 (3)
C2—N1—C7—C6	−71.3 (3)	N4—C3—C31—C311	61.2 (3)
C7—N1—C2—C21	−166.1 (2)	N4—C3—C31—C312	−65.0 (3)
C7—N1—C2—C3	68.9 (3)	C31—C3—N4—C5	−162.7 (2)
N1—C2—C3—N4	−78.7 (3)	C3—N4—C5—C6	−7.1 (4)
C21—C2—C3—C31	37.9 (3)	C3—N4—C5—O5	176.3 (2)
C21—C2—C3—N4	161.4 (2)	N4—C5—C6—C7	−61.4 (3)
C2—C3—C31—C311	−174.3 (2)	O5—C5—C6—C7	115.1 (3)
C2—C3—C31—C312	59.5 (3)	C5—C6—C7—N1	83.0 (3)

Structure solution was by direct methods *SHELXS*86 (Sheldrick, 1985). Refinement was by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). All the non-H atoms were refined with anisotropic displacement parameters and H atoms were inserted at a distance of 0.950 (2) Å from the C atoms using a riding model, with displacement parameters equal to 1.1 × U_{eq} of their respective carrier atoms.

AT and UPS thank the University Grants Commision and Department of Atomic Energy, respectively, for the award of fellowships. DST is acknowledged for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71711 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1061]

References

Baliah, V., Lakshmanan, MR. & Pandiarajan, K. (1978). *Indian J. Chem.* **16B**, 72–73.

Hamor, H. A. & Martin, I. L. (1984). *X-ray Crystallography and Drug Action*, edited by A. S. Horn & C. J. De Ranter, pp. 275-301. Oxford: Clarendon Press.

Mohan, R. S. (1985). PhD thesis, Univ. of Annamalai, Tamilnadu, India. Unpublished.

Priya, V., Shamala, N., Viswamitra, M. A., Senthilkumar, U. P. & Jeyaraman, R. (1992). *Acta Cryst.* C**48**, 1048-1051.

Senthilkumar, U. P. & Jeyaraman, R. (1993). *Tetrahedron Lett.* Submitted.

Senthilkumar, U. P., Jeyaraman, R., Murray, R. W. & Singh, M. (1992). *J. Org. Chem.* **57**, 6006–6014.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.